Calcium Chloride

Crops

Identification of Petitioned Substance

Chemical Names:
calcium chloride anhydrous
calcium chloride dihydrate
calcium chloride hexahydrate
calcium chloride tetra hydrate

Other Names:
calcium dichloride (anhydrous)
calcium (II) chloride

Trade Names:
Peladow
Liqidow
Dowflake
Combotherm
Briners Grade Calcium Chloride
E XPRESS® Calcium Chloride
EXPRESS® Calcium Chloride
EXPRESS® RM Calcium Chloride;
EXPRESS® RM Calcium Chloride
TETRA 94™ Calcium Chloride
liquid calcium chloride
technical grade calcium chloride
NSF Grade Calcium Chloride
WinterThaw® DI Calcium Chloride

CAS Numbers:
10043-52-4 (anhydrous)
10035-04-8 (dihydrate)
7774-34-7 (hexahydrate)
25094-02-4 (tetrahydrate)

Other Codes:
233-140-8 (EINECS number; dihydrate)
509 (INS number; food additive used as a firming agent, stabilizer, and thickener)

Characterization of Petitioned Substance

<u>Composition of the Substance</u>:
Calcium chloride is an inorganic salt composed of calcium and chlorine with the chemical formula CaCl. There are several forms of calcium chloride, including the anhydrous and hydrate (e.g., monohydrate [$CaCl \cdot H_2O$], dihydrate [$CaCl \cdot 2H_2O$], tetrahydrate [$CaCl \cdot 4H_2O$], and hexahydrate [$CaCl \cdot 6H_2O$]) forms. Hydrates are substances that form crystals containing water molecules when aqueous substances are evaporated. The water can be removed by heating. Different forms of calcium chloride have varying percentages of calcium chloride, including: pure calcium chloride (100 percent), monohydrate (86.03 percent), dihydrate (75.49 percent), tetrahydrate (60.63 percent), and hexahydrate (50.66 percent) (DOW 2001).

<u>Properties of the Substance</u>:
Calcium chloride is a white, odorless, crystalline salt (Mallinckrodt Chemicals 2005, Webelements 2006). It reacts readily with water resulting in the aforementioned hydrate forms. The melting points, boiling points, and density for the different forms of calcium chloride decrease with the increasing water content (DOW 2001).

<u>Specific Uses of the Substance</u>:

In agriculture, calcium chloride is used as post-harvest treatments and foliar sprays to increase the yield and calcium content of the fruit and decrease the incidence of physiological disorders related to calcium deficiencies. Calcium is necessary for plants in order to strengthen cell walls and maintain membrane integrity. Although calcium chloride may be used as a soil amendment, if approved, to provide a supplemental source of calcium to the plant, calcium does not move freely within the plan and is not readily translocated to the growing tips. Nutritional calcium deficiency can lead to several physiological disorders including distortion of young leaves, curled margins, tips hooked back on young leaves, irregular or ragged shape of young leaves, brown spotting or scorching of young leaves, death of terminal buds, poorly developed root systems, and fruit quality problems. Examples of fruit quality problems include blossom-end-rot in tomatoes, peppers and melons; bitter pit in apples; twins in pineapples; internal browning in pineapples; tip-burn in lettuce; and internal brown fleck in potatoes (HortResearch 2006, Napier and Combrink 2006).

Calcium chloride is also used for the following purposes (DC Chemical Co., Ltd. 2001, DOW 2006):

- deicing agents – for sidewalk, parking lot, and road treatments;
- road stabilization and dust control agents;
- industrial processing – as additives in plastics, for calcium salt production, drainage aids for wastewater treatment;
- accelerators in concrete – to increase curing speed;
- oil and gas well fluids – to boost the efficiency of drilling and the completion of wells; and
- miscellaneous smaller applications – tire ballast, water treatment, hydrocarbon desiccant, refrigeration brine, food processing agent or coagulating agent and additive for foods.

Approved Legal Uses of the Substance:

Calcium chloride is included on the National List (§205.602 (c)) as a nonsynthetic substance prohibited for use in organic crop production with the following specification: the "brine process is natural and prohibited for use except as a foliar spray to treat a physiological disorder associated with calcium uptake."

Calcium chloride is "Generally Recognized as Safe" (GRAS) by the U.S. Food and Drug Administration (FDA). According to the FDA, calcium chloride is acceptable for use in foods at levels not to exceed current good manufacturing practices. Additionally, the average intake of calcium chloride as food additives has been estimated to be 160-345 mg/day for individuals (DOW 2006, FDA 2004).

Calcium chloride is not regulated by the EPA; no information was found in EPA's Envirofacts Master Chemical Integrator (EMCI) (EPA 2002).

The Washington State Department of Agriculture: European Organic Verification Program (EOVP) allows use of calcium chloride in organic food production only if used as a foliar spray after identification of physiological disorders associated with calcium uptake (WSDA/EVOP 2006).

Action of the Substance:

When applied as a foliar spray or used as a post-harvest dip for the fruit, calcium chloride acts as a calcium supplement to plants with nutrient deficiencies. Calcium becomes available for transport, which can help increase the calcium content and yield of fruit and decrease the incidence of disorders (Autio and Bramlage 2001).

In soils, calcium chloride would serve two functions due to its calcium content. First, calcium chloride could be used as a fertilizer to increase and maintain levels of calcium in the soil, thereby supplementing the plant with this necessary nutrient. Second, calcium chloride could improve soil structure by flocculating soil particles (i.e., grouping them together) and creating a larger distribution of soil pores. Larger pores make the soil more water permeable, thus enhancing the movement of water and nutrients through the soil; smaller pores increase the holding capacity of soil making water more available for plant uptake. Additionally, calcium chloride used in this manner promotes the growth of soil organisms that help increase and maintain the stability of the soil structure. Improvements in soil structure also result in an increase of water infiltration, soil-air gas exchange, root penetration, and seedling emergence (HortResearch 2006, Mishra 2004).

Status

International

As of June 2004, the **Canadian General Standards Board** accepted calcium chloride for use as a soil amendment or crop aid only if it is derived from a natural source (CGSB 2004). It is allowed for foliar use to correct bitter pit in apples and on crops that are susceptible to end rot. It is also allowed for restricted for use on other crops where a deficiency has been documented. In addition, the Ontario Ministry of Labour has established an occupational exposure limit (OEL) for calcium chloride of 5 mg/m^3 and a maximum intake of 50 mg/day calcium chloride via dust inhalation under the OEL (UNEP 2002).

The **CODEX Alimentarius Commission**, which implements the Joint FAO/WHO Food Standards Programme, includes calcium chloride as an acceptable food additive for fruits and vegetables and soybean products in regards to organic labeling (FAO/WHO 2001). In addition, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) evaluated calcium chloride as a food substance and determined it to be of very low toxicity; therefore, the establishment of an acceptable daily intake for calcium chloride was determined to be unnecessary (UNEP 2002).

European Economic Community (EEC) Council Regulation 2092/91 allows the use of calcium chloride as a foliar treatment of apple trees, after identification of physiological disorders associated with calcium uptake. Need recognized by the inspection body or inspection authority (Organic Trade Association 2002).

Evaluation Questions for Substances to be used in Organic Crop or Livestock Production

Evaluation Question #1: Is the petitioned substance formulated or manufactured by a chemical process? (From 7 U.S.C. § 6502 (21))

Calcium chloride can be formed by three processes, two chemical and one natural—the hydrochloric acid process, the Solvay process, and the natural brine process, and which are described below (FDA 2004, Morris Chemicals 2005, TETRA Technologies 2005).

The Hydrochloric Acid Process

The hydrochloric acid process potentially produces the purest synthetic calcium chloride. This process involves treating limestone with hydrochloric acid to form calcium chloride and carbonic acid, H_2CO_3, which is subsequently converted into carbon dioxide and water, as follows:

$$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O$$

The purification process of the calcium chloride requires the addition of milk of lime[1], similar to the natural brine process described below, to precipitate out any magnesium that may be in the initial calcium chloride product.

Furthermore, the purity of the calcium chloride is dependent on the purity of the hydrochloric acid. For example, if concentrated hydrochloric acid is used (≈36 percent HCL), the resulting concentration of calcium chloride in the solution will also be approximately 36 percent (TETRA Technologies 2005).

[1] Milk of lime is suspension of fine calcium hydroxide, $Ca(OH)_2$, particles in water.

The Solvay Process

The Solvay process is the most common chemical process used for the production of synthetic calcium chloride. However, the main purpose of the Solvay process is to produce sodium carbonate (TETRA Technologies 2005). The Solvay process involves an initial reaction of sodium chloride from salt deposits, ammonia, limestone, and water to produce sodium bicarbonate, ammonium chloride, and calcium oxide, as follows:

$$NaCl + NH_3 + CaCO_3 + H_2O \rightarrow NaHCO_3 + NH_4Cl + CaO$$

The solid sodium bicarbonate is then filtered out and converted to sodium carbonate by heating, recovering some of the carbon dioxide from the initial step of the process:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

The last step in the Solvay process involves the reaction of ammonium chloride and calcium oxide that formed from the hydration of lime that was derived by heating the limestone in the first reaction. This final reaction results in the production of calcium chloride, water, and ammonia:

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

The recovered ammonia and carbon dioxide are recycled back to the initial brine solution and reused (Kiefer 2002).

The Brine Process

The brine process involves concentrating calcium chloride in naturally occurring brines, or strong saline solutions that are pumped out from salt lakes and salt deposits. In addition to calcium chloride, natural brine solutions often contain other chlorides (e.g., magnesium chloride, sodium chloride). The calcium chloride concentration process involves adding milk of lime to the brine, which results in the precipitation of magnesium in the form of magnesium hydroxide, $Mg(OH)_2$. Following filtration, water is evaporated from the calcium chloride solution causing sodium chloride to precipitate out of the solution because it is less soluble than calcium chloride, resulting in a crystalline salt (DOW 2006, Morris Chemicals 2005, TETRA Technologies 2005). The final commercial products have varying concentrations of calcium chloride and may contain other salts such as sodium chloride, potassium chloride, and strontium chloride (Mallinckrodt Chemicals 2004).

One chemical manufacturer also produces "untreated" calcium chloride that also involves extracting naturally occurring brines, or strong saline solutions, from salt lakes and salt deposits. This solution is collected in segregated storage ponds where it is further concentrated by solar evaporation until it achieves a marketable concentration (TETRA Technologies 2001).

Evaluation Question #2: Is the petitioned substance formulated or manufactured by a process that chemically changes the substance extracted from naturally occurring plant, animal, or mineral sources? (From 7 U.S.C. § 6502 (21).)

Of the three production processes described in Evaluation Question #1, only the brine process involves extraction of calcium chloride from a naturally occurring source. The brine process includes processing steps that precipitate undesirable compounds from the brine. These steps do not chemically alter the calcium chloride. The other two processes involve chemical change of substance, some of which (e.g., limestone) occur naturally.

Evaluation Question #3: Is the petitioned substance created by naturally occurring biological processes? (From 7 U.S.C. § 6502 (21).)

Calcium chloride exists naturally in the environment and can be obtained from salt lakes and salt deposits through the use of the brine process (see Evaluation Question #1). However, the process used to extract calcium chloride from natural materials for commercial applications does not occur in nature. The hydrochloric acid and Solvay processes for generating calcium chloride are not naturally occurring biological processes.

Evaluation Question #4: Is there environmental contamination during the petitioned substance's manufacture, use, misuse, or disposal? (From 7 U.S.C. § 6518 (m) (3).)

As described in Evaluation Question #1, the chemical manufacturing process for calcium chloride requires the extraction of either sodium, limestone, or both from natural sources. Chemical reactions are involved in the production of calcium chloride. However, all manufacturing processes are conducted in closed production systems (UNEP 2002). In addition, many of the reagents and products are recycled or used for other purposes after calcium chloride formation. For example, the ammonia and carbon dioxide utilized in the Solvay process are recycled back to the initial brine solution for reuse. Furthermore, the magnesium hydroxide and sodium chloride precipitates from the hydrochloric acid and natural brine production processes are used to prepare other compounds (e.g., table salt, other magnesium salts) (UNEP 2002).

Based on the petitioned use of calcium chloride as a foliar spray, post-harvest dip, or soil amendment no information was available to suggest that environmental contamination will result from these uses. However, improper disposal of spent solutions after foliar applications or post harvest dips may potentially affect surface waters and aquatic organisms by increasing the calcium and chloride content of the water (UNEP 2002).

Evaluation Question #5: Is the petitioned substance harmful to the environment? (From 7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i).)

In water, calcium chloride readily disassociates into calcium and chloride ions, both of which exist naturally in the aquatic environment. Their concentrations in surface water depend on various factors, such as geological parameters, weathering, and human activities. Toxic effects are observed in aquatic organisms at high exposure levels (>1,000 mg/L). Acute and prolonged toxicity has been observed in fish[2] (96-hour LC_{50} = 4,630 mg/L for the fathead minnow), aquatic plants/algae[3] (72-hour EC_{20} = 1,000 mg/L [biomass] for algae [*Selenastrum capricornutum*]), and invertebrates (96-hour EC_{50} = 780 mg/L, [immobilization] for the sludge worm [*Tubifex tubivex*]) (UNEP 2002).

In soil, calcium chloride is not readily absorbed in soil due to its solubility and affinity for dissociation. Instead, the ions may act as free ions or form stable inorganic or organic salts complexes with other ions. Additionally, the calcium ion may bind to soil particulate, while the chloride ion, which is more mobile and soluble in water, may drain into surface waters (UNEP 2002).

As noted previously, calcium chloride obtained from natural brine sources may contain a significant amount of sodium chloride and other inorganic chloride salts. Thus, damage to vegetation may occur due to the absorption of salt splashed on foliage and the deposition of chloride in soil resulting in the uptake and subsequent accumulation of chloride in the plant. This could potentially lead to tipburn, browning, and chlorosis of foliage (UNEP 2002).

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[2] An LC_{50} is the concentration of a pollutant or effluent at which 50 percent of the test organisms die and is a common measure of acute toxicity (EPA 2006).

[3] An EC_{50} is the concentration of a pollutant or effluent in an environmental medium expected to produce a certain effect in 50 percent of the test organisms in a given population under defined conditions (SIS 2005).

Calcium chloride is not expected to accumulate in living organisms or produce hazardous byproducts from photolysis or biodegradation in the environment (Environment Canada 1981, UNEP 2002).

Evaluation Question #6: Is there potential for the petitioned substance to cause detrimental chemical interaction with other substances used in organic crop or livestock production? (From 7 U.S.C. § 6518 (m) (1).)

Based on calcium chloride's petitioned use as a foliar spray or post harvest dip, no information was uncovered to suggest that calcium chloride could cause detrimental chemical interaction with other substances used in organic crop production.

Evaluation Question #7: Are there adverse biological or chemical interactions in the agro-ecosystem by using the petitioned substance? (From 7 U.S.C. § 6518 (m) (5).)

Calcium chloride obtained from natural brine sources may contain a significant amount of sodium chloride and other inorganic chloride salts. Damage to vegetation may occur due to the absorption of salt splashed on foliage and the deposition of chloride in soil resulting in the uptake and subsequent accumulation of chloride in the plant. This could potentially lead to tipburn, browning, and chlorosis of foliage (UNEP 2002).

Evaluation Question #8: Are there detrimental physiological effects on soil organisms, crops, or livestock by using the petitioned substance? (From 7 U.S.C. § 6518 (m) (5).)

Because calcium is an essential nutrient, the addition of calcium to soil from the petitioned uses is unlikely to adversely affect the survival and function of soil organisms such as earthworms, mites, grubs, bacteria, nematodes, algae, and protozoa. However, high levels of chloride ion may have the potential to impact organisms in soil. In addition, as mentioned previously, calcium chloride obtained from natural brine sources may contain a significant amount of sodium chloride and other inorganic chloride salts, which could result in damage to vegetation from the uptake of these inorganic salts and subsequent chloride accumulation in the plant and soil (UNEP 2002). Available information does not identify concentrations of calcium and chloride ion concentrations in soil likely to result from the proposed uses, or whether those concentrations would approach ecological benchmark concentrations for terrestrial organisms.

Evaluation Question #9: Is there a toxic or other adverse action of the petitioned substance or its breakdown products? (From 7 U.S.C. § 6518 (m) (2).)

As noted previously, calcium chloride readily disassociates into calcium and chloride ions when released into the environment. Both of these ions are essential nutrients for higher plants. For example, calcium plays a vital role in strengthening cell walls and plant tissues, reducing the toxicity of soluble organic acids, and elongating roots; chloride is important to plants for the photosynthesis and osmoregulation processes (UNEP 2002).

Nonetheless, acute toxicity has been reported in fish, aquatic plants/algae, and invertebrates (see Evaluation Question #5) resulting from exposure due to additional calcium chloride added to the system (UNEP 2002). In addition, damage to vegetation may occur due to the absorption of salt splashed on foliage and the deposition of chloride in soil resulting in the uptake and subsequent accumulation of chloride in the plant. However, the impact of calcium chloride on plants is expected to be minimal compared to other chloride-containing agents (UNEP 2002).

Evaluation Question #10: Is there undesirable persistence or concentration of the petitioned substance or its breakdown products in the environment? (From 7 U.S.C. § 6518 (m) (2).)

In the presence of water, calcium chloride readily decomposes into calcium and chloride ions and is extremely mobile. According to its Material Safety Data Sheets (MSDS), calcium chloride does not bioaccumulate in the aquatic environment. Thus, the product and its breakdown products are not likely to have an undesirable persistence in the environment (DOW 2006, UNEP 2002).

<u>Evaluation Question #11:</u> **Is there any harmful effect on human health by using the petitioned substance? (From 7 U.S.C. § 6517 (c) (1) (A) (i), 7 U.S.C. § 6517 (c) (2) (A) (i)) and 7 U.S.C. § 6518 (m) (4).)**

In general, there is a potential for both indirect and direct exposure of humans to calcium chloride. Calcium chloride, or its dissociated ions, is commonly found in drinking water and foods (UNEP 2002).

Although calcium chloride is included on FDA's GRAS list (FDA 2004), ingestion of concentrated or pure calcium chloride products may cause gastrointestinal irritation or ulceration (DOW 2006). Furthermore, skin and eye exposure to calcium chloride can lead to irritation and burns. While vapors are unlikely due to physical properties, dust or mists may cause irritation to the upper respiratory tract.

<u>Evaluation Question #12:</u> **Is there a wholly natural product which could be substituted for the petitioned substance? (From 7 U.S.C. § 6517 (c) (1) (A) (ii).)**

Natural products that may substitute for calcium chloride in its petitioned use as a source of calcium include nonsynthetic fertilizers and soil amendments containing calcium. These fertilizers provide a source of calcium, as well as a balance of nitrogen-phosphorous-potassium (N-P-K), sulfur, magnesium, iron, trace minerals, and micronutrients and have a complete and predictable release of nutrients (Nature Safe 2006a). However, many of these fertilizers have low calcium content (Nature Safe 2006b). In addition, alternate natural forms of calcium could be used such as limestone, lime, gypsum, dolomite, rock phosphate, or bonemeal (Pacific Calcium 2006, TETRA Technologies undated). Eggshells and oystershells can also be ground up to form natural granular calcium supplements (MSU 2002, Nyerges and Nyerges 1998).

<u>Evaluation Question #13:</u> **Are there other already allowed substances that could be substituted for the petitioned substance? (From 7 U.S.C. § 6518 (m) (6).)**

According to the U.S. Department of Agriculture (USDA) National Organic Program (NOP) rule §205.601(j), other allowed plant or soil amendments that could provide calcium include the following:

- **Humic acids** (USDA 2006a) - During warm weather, plants use calcium faster than it can be transferred to their off shoots. This results in a deficiency despite the fact that calcium is being absorbed by the roots. With the addition of fulvic acid, a humic substance, calcium becomes attached to the fulvic acid chain. This causes the calcium to move more freely within the plant, subsequently reducing the incidence of tip burn (Biksa 2002, Kelley 2004). In addition, some humic acid products aid plants with the uptake of micronutrients, including calcium (Kelley 2004).
- **Aquatic plant extracts (other than hydrolyzed)** (USDA 2006b) - Calcified seaweed and kelp are calcium sources useful on acidic or alkaline soils (Baker 1996, Sauls et al. undated).
- **Liquid fish products** (status unknown) - Some products contain small percentages of calcium (Baker 1996).

Additionally, lime mud is scheduled for NOP evaluation as an allowed plant or soil amendment under the NOP rule §205.601(j) (USDA 2004).

<u>Evaluation Question #14:</u> **Are there alternative practices that would make the use of the petitioned substance unnecessary? (From 7 U.S.C. § 6518 (m) (6).)**

Potential alterative practices for increasing fertility of soil and availability of nutrients for plants, include recycling compost or other sources of nutrients. Alternative soil building practices include using cover crops, compost and/or manures, reducing tillage, avoiding traffic on wet soils, and maintaining soil cover with plants and/or mulches (Feenstra et al. 1997). However, these alternative practices do not increase the translocation of calcium to the growing tips of the plant.

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